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Synthesis of mesoporous carbons of high surface area and porosity by using polymer blends as template

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Abstract In this paper, we provided a new method to generate the carbonizable polymer–silica nanocomposite in one step by using different polymer blends of phenol formaldehyde (PF) and silica-gelling polymer (i.e., Pluronic F127, PEO6000 or gelatin) as the template. The PF–silica gelling polymer–silica nanocomposite was obtained from fast silicification in a highly diluted silica solution at pH≈5.0. Because the PF, one kind of carbon sources, was embedded in the as-synthesized nanocomposite, the mesoporous carbon was easily obtained from pyrolysis at 1,000°C and silica removal by diluted HF solution. The resulted mesoporous carbons possess a high surface area of 780–1,500 $m^2 g^{-1}$ and large pore size of 2.6–13.7 nm. In addition, the morphology of the mesoporous carbons can be tailored to nano-sized particles and hollow spheres by using different silica gelator–PF polymer blends. In practice, the electrically conducting mesoporous carbons of high surface area and large pore size can be considered as good material for preparing the supercapacitor. The mesoporous carbons exhibit electric capacity of 75–158 Fg^{-1} in 2.0 M H_2SO_4 electrolyte solution at scan rate of 1–50 mVs^{-1}.

Keywords Polymer blend · Mesoporous carbon ·
Mesoporous silica · Electric double-layer capacitor

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Introduction

Mesoporous carbons of high surface area, porosity, and good electric conductivity have been widely used as the material for supercapacitor and electrode of the direct methanol fuel cell [1]. Typically, the nanocasting strategy was utilized to prepare the ordered mesoporous carbons (OMCs) with different mesostructures and morphologies by using mesoporous silicas with well-ordered and 3D-interconnected mesostructures as hard template [2]. For example, a series of OMCs, namely CMK-1, CMK-3, and CMK-5, were templated by MCM-48, SBA-1, and SBA-15, respectively [3–8]. However, the mesoporous silica-templating method to prepare mesoporous carbons includes many procedures, such as mesoporous silica preparation, surfactant removing by calcinations, introduction of carbon precursor and catalytic sites, polymerization of the carbon precursor, pyrolysis, and silica removal. The whole synthetic processes takes about 2–3 days and wastes much energy to remove the expensive organic template. Moreover, the carbon monomer-type carbon source such as sucrose and furfuryl alcohol needs polymerization in the

nanochannels to cast the mesostructure of the mesoporous silica. Because the complete polymerization in the nanochannels is not easily to control, doubly or triply repeating impregnation and polymerization were required for achieving whole replication of the mesostructure and morphologies [6–8]. Although other suitable carbon precursors (i.e., mesophase pitches, phenol-formaldehyde, polyacrylonitrile) have been used to prepare the mesoporous carbons, there are many time- and energy-consuming procedure in the *exo*-templating nanocasting method.

To avoid the complicated process including synthesis of surfactant–silica composite, surfactant-removal, carbon source introduction, an effective *endo*-templating method by using carbon source as the template of the mesoporous silica is much desired [9]. A polyethylene oxide-*b*-polyacrylonitrile di-block copolymer containing the carbonizable polyacrylonitrile segment was used as template to form the mesoporous carbon in high efficient, but the synthesis of the PAN-PEO di-block copolymer is still costly and time-consuming [10]. Based on the polymer chemistry [11], it is well known that thermosetting phenol formaldehyde polymer (PF) has been widely used as carbon precursors in industry. Owing to the PF polymer possessing lots of hydroxyl groups (i.e., $-CH_2OH$ and C_6H_6-OH: hydrogen-bonding donor), it has a high affinity to blend homogeneously with water-soluble polymers having the hydrogen-bonding donors or acceptors. In addition, among the water-soluble polymers, it is known that the polyethylene oxide-based polymers or copolymers with the ether groups (i.e., $-O-$, hydrogen-bonding acceptor) or the natural polymer gelatin with the amide groups ($-CO-NH_2$) can have a capability to aggregate with silica species and act as silica gelator to increase the silica condensation rate through hydrogen-bonding interactions at pH value less than 7.0 [12]. Based on these concepts, it is reasonably supposed that PEO-based polymers or gelatin could blend with the PF polymers to form a homogeneously miscible polymer blend as a novel template of the porous silica. Therefore, in this study, we preformed three different polymer blends (i.e., PF-PEO6000, PF-F127, and PF-gelatin) in a water–ethanol solution to combine with a stock silicate solution at pH≈5.0. Owing to the synergistic silica gelator–PF–silica composites containing carbonizable PF polymer and silica, mesoporous carbons in different forms were prepared after pyrolysis and silica removal, and mesoporous silicas were obtained from hydrothermal treatment and calcination in air. In addition, the morphology of the mesoporous carbons can be tailored to hollow spheres and fine particles by using different silica-gelling polymer. Distinct from other methods, using the cheap PF, silica-gelling polymer and sodium silicate provided a cost-effective synthetic way to produce the mesoporous carbons for testing their potential applications.

Materials and methods

Materials

The silica source is sodium silicate (27 wt% SiO_2, 14 wt% NaOH, Aldrich). The organic templating agents are nonionic triblock copolymer Pluronic F127 ($EO_{106}PO_{70}EO_{106}$), homopolymer PEO6000 (polyethylene oxide), and natural polymer gelatin were purchased from Aldrich. The sulfuric acid (H_2SO_4) is from Acrôs. The resol-type phenol-formaldehyde PF2180 (PF; phenol/formaldehyde=0.8–0.9; M_W about 96,000, Chang-Chung Plastics, Taiwan) is used as carbon source. The ethanol (95 wt%) is from Acrôs. All commercial chemicals were used directly without further purification.

Synthesis of mesoporous carbon by using polymer blend

The typical synthetic process for the PF–silica gelator–silica nanocomposite is as follows: 2.0 g of silica gelator polymer (e.g., Pluronic F127, PEO6000 or gelatin) and 2.0 g of PF polymer was dissolved in a mixture of 20.0 g ethanol and 10.0 g water to form a clear solution. Then, the PF–silica gelator polymer blend solution was poured quickly into an acidified sodium silicate solution aqueous solution of pH≈5.0 at 40 °C. The stock silicate solution was prepared by adjusting the pH value of a mixture of 8.0 g of sodium silicate (27 wt% SiO_2, Aldrich) and 300.0 g of water to 5.0 and aging for 5–10 min. A light-yellowed precipitate was formed within few seconds. Filtration, washing, and drying at 100 °C gave the PF–silica gelator–silica nanocomposite. After that, the mesoporous carbons with disordered mesostructures were gained via a pyrolysis at 1,000 °C under N_2 atmosphere for 2 h and silica removal by 6 wt% HF-etching. Because HF solution is highly toxic and dangerous to use, one must be very careful during silica removal process.

Electrochemical tests

Two-electrode capacitor cell was fabricated to examine the electrochemical performance of the mesoporous carbon electrode in a capacitor. To prepare the mesoporous carbon electrode, a proper amount of carbon (≈ 5.0 mg) was ground with 100 mg of 0.825 wt% polytetrafluoroethylene (PTFE) as binder and pressed between two pieces of stainless steel plates under 3,000 psi. The cell was assembled with two facing mesoporous carbon electrodes, sandwiching a piece of filter paper as separator. Thereafter, the electrode was dried overnight at 80 °C. Before electrochemical tests, the electrode was soaked in 2.0 M H_2SO_4 aqueous solution and sonicated for 20 min to guarantee that the electrode material was thoroughly wetted

by electrolyte. Afterwards, the wetted electrode was characterized electrochemically in a 2.0 M H$_2$SO$_4$ aqueous solution using an Ag/AgCl reference electrode. Cyclic voltammetric measurement was conducted on a Won A Tech WBSC 3000 analyzer within −1.0 and 1.0 V at different sweep rates in 2.0 M H$_2$SO$_4$.

Characterization

N$_2$ adsorption–desorption isotherms were obtained at 77 K on a Micromeritics ASAP 2010 apparatus. Before analysis, the sample was degassed at 120 °C for about 6 h in 10^{-3} Torr. The pore size distribution was obtained from the analysis of the adsorption branch by using the Barrett-Joyner-Halenda (BJH) method. The scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images were taken on an S-800 (Hitachi) operated at an acceleration voltage of 20 KeV and an H-7500 (Hitachi) operated at 100 KeV, respectively. Thermogravimetric analysis (TGA) tests were conducted with a TA Q-50 thermogravimetric system. In a typical experiment, about

10 mg of the sample was heated to 700–800 °C at 10 °C/min in air. The organic content was estimated from the weight loss between the temperature ranges of 140–500 °C.

Results and discussion

Mesoporous carbon synthesized with F127-PF polymer blend

Figure 1a shows the TGA curves of the F127–PF–silica composite and the mesoporous carbon from F127–PF–silica composites. From TGA curve of the F127–PF–silica composite, one can clearly see that the organic percentage is about 45 wt%. The high organic content in the composites indicates that the polymer blend can be embedded in the silica via the fast sol-gel reaction. Because the PF–F127–silica composite contains the carbonizable PF polymer, the mesoporous carbon, thus, can be effortlessly obtained from a high-temperature pyrolysis and silica removal by HF etching. The TGA curve of the mesoporous

Fig. 1 a TGA curves of the PF-F127-silica composite (*curve I*) and the resulted mesoporous carbon (carbon II); b low-magnification TEM image of the mesoporous carbon. c High-magnification TEM image of the mesoporous carbon. d N$_2$ adsorption–desorption isotherm of the mesoporous carbon. *Arrow* indicates the additional absorption from the hollow interior of the carbon hollow sphres (*scale bar*=100 nm)
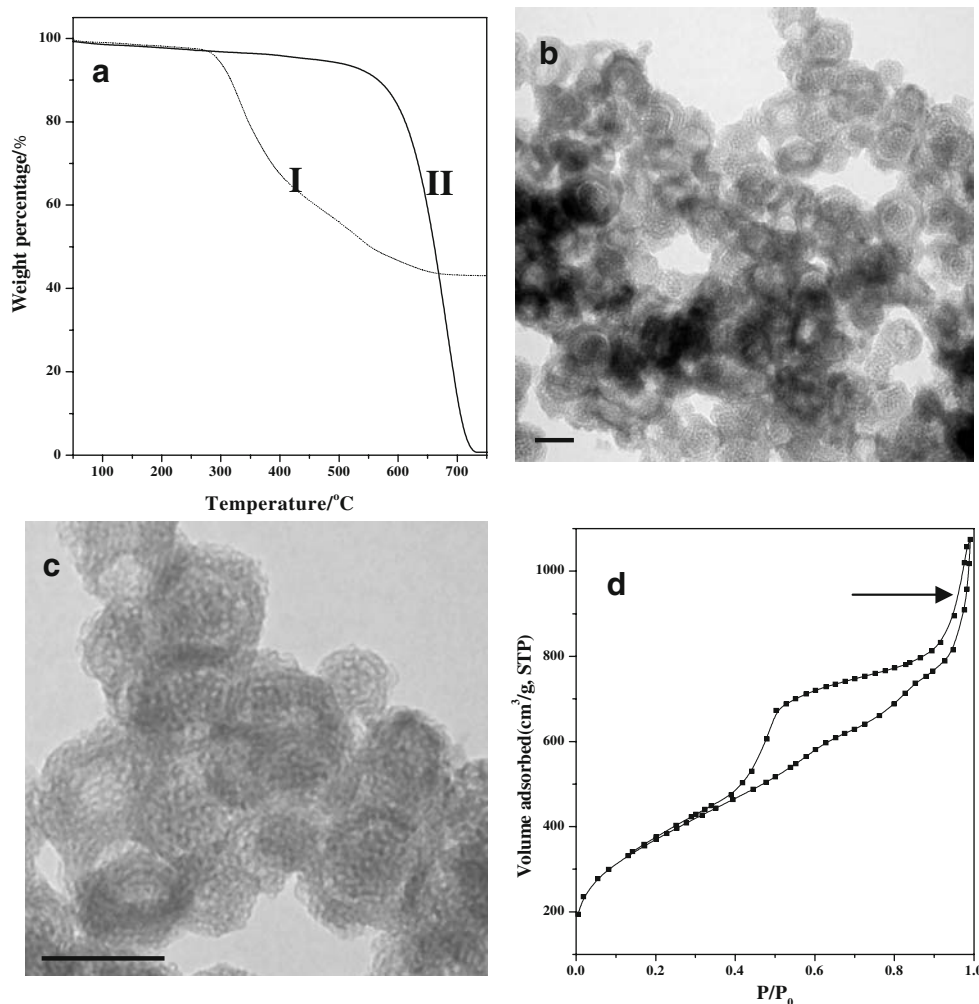
carbon demonstrates a sharp weight-loss curve at a combustion temperature at around 650 °C (Fig. 1a), which indicates that the F127–PF resin blend can be converted to a phase-homogeneous and thermally stable carbon as well as those form other carbon sources [13]. In addition, a low-weight percentage of inorganic residue (<1.5 wt%) implies a nearly complete removal of the silica by HF-etching.

According to the TEM observation on the prepared mesoporous carbon (Fig. 1b, c), we found that the sample's morphology is sphere-like and the size is around 100 nm. High-magnification TEM image obviously demonstrates the disordered mesostructure and the pore size of about 7.0 nm. Some of the carbon spheres are hollow. The N_2 adsorption–desorption isotherm of the mesoporous carbon exhibit a capillary condensations at P/P_0 from 0.6 to 0.8. (Figure 1d). As is typical of mesoporous materials, the mesoporous carbon have a high BET surface area of 1502 m^2 g^{-1} large pore size of 7.0 nm calculated by BJH method and pore volume of 1.8 cm^3 g^{-1}). Due to the presence of the hollow interior of the hollow spheres, it is noteworthy that the PF resin-F127-templated mesoporous silica demonstrates addition absorption at $P/P_0 \approx 0.9$. The mesoporous carbon possesses bi-model pores. Consequently, using the PF–

F127 polymer blend provides a new *endo*-templating method to conveniently synthesize the mesoporous carbon.

In this study, we tried to explain the formation mechanism of the PF–F127–silica nanocomposite. Based on the concept of polymer-blending [11], neutral Pluronic F127 tri-block copolymers can readily blend with other polymers via hydrogen-bonding interaction. Therefore, a miscible polymer blend solution of F127 block-copolymer and PF resin can be readily formed through multiple hydrogen bonding between hydroxyl groups (–OH) or hydroxylmethylene groups(–CH₂OH) of the PF resin and ether groups(–O–) in the F127 copolymer [14, 15]. In the F127–PF polymer blend, the F127 parts have an affinity to aggregate with silica species via hydrogen-bonding inter-action at pH≈5.0 [12], and the hydrophobic PF resin incorporates into the hydrophobic part of the F127 copolymer to form a F127–PF resin blending micelles. After fast assembling with the silica species at pH value of about 5.0, a F127–PF–silica composite with disordered mesostructure was thus obtained. Because the F127–PF–silica composite is composed of the inorganic silica and the thermosetting PF resin, it is readily converted to carbon via a high-temperature pyrolysis. On the other hand, calcination

Fig. 2 a TGA curves of the PF–PEO6000–silica composite (*curve I*) and the resulted mesoporous carbon (carbon II); b low-magnification TEM image of the mesoporous carbon. c High-magnification TEM image of the mesoporous carbon. d N_2 adsorption–desorption isotherm of the mesoporous carbon. *Arrow* indicates the additional absorption from the hollow interior of the carbon hollow spheres
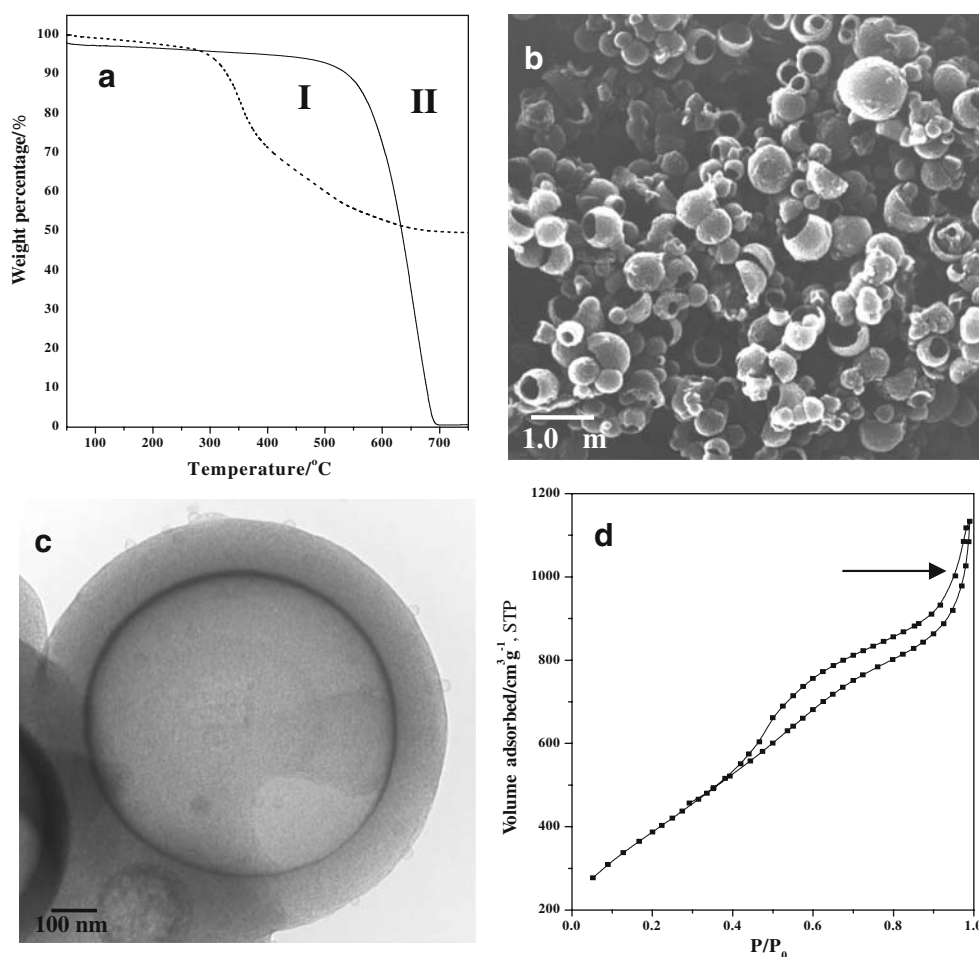
in air produced mesoporous silica with high surface area and large pore size as desired.

## Mesoporous carbon synthesized with PE6000O–PF polymer blend

The basic concept of the polymer-blending template can be widely applied to other polymer–PF resin composites. Based on the silica chemistry [12], the cheap and low-toxicity PEO homopolymers with the ether oxygen atoms ($-O-CH_2-CH_2-$, hydrogen-bonding acceptor) have a high affinity both to PF polymer and to silanol groups (Si–OH, hydrogen-bonding donor) of silicate species via multiple hydrogen-bonding interactions in the solution of about neutral pH value at room temperature. Thus, a PEO6000-PF polymer blend was used to synthesize the mesoporous carbon as well.

As that of PF–F127–silica component, the TGA curve of the PF–PEO6000–silica nanocomposite reveals that the organic content is close to 50 wt% (Fig. 2a), which demonstrates a high organic content PEO6000 and PF polymer blend embedded in the mesostructural silica. After

pyrolysis at 1,000 °C and silica removal, the prepared mesoporous carbon exhibits significant weight loss in a narrow temperature range between 600 and 650 °C. Thus, the porous carbon of high thermal stability can be easily produced from the PF–PEO6000–silica composite. The silica residue in the porous carbon is less than 2.0 wt%, indicating that the silica was almost entirely removed by HF-etching.

Figure 2b shows the representative SEM image of the mesoporous carbon synthesized with the PEO6000–PF blend. It can be clearly seen that the particle's morphology is spherical, and the diameter of the spherical ranges from 1.0 to 0.5 μm. Some broken spheres reveal that the spheres are hollow, and the wall thickness is around 0.1 μm. The hollow interiors of the carbon spheres can be more clearly shown in a high-magnification TEM image (Fig. 2c). The shell thickness of the hollow mesoporous carbon spheres is around 100 nm. The TEM image clearly shows that the mesostructure of the hollow sphere's shell is wormhole like (i.e., interconnected), and the pore size is around few nanometers. In parallel to the TEM observations, the hollow mesoporous carbon spheres exhibit a type IV N_2

Fig. 3 **a** TGA curves of the PF–gelatin–silica composite (*curve I*) and the resulted mesoporous carbon (carbon II); **b** low-magnification TEM image of the mesoporous carbon. **c** High-magnification TEM image of the mesoporous carbon. **d** N_2 adsorption–desorption isotherm of the mesoporous carbon. *Arrow* indicates the additional absorption from the hollow interior of the broken carbon hollow sphres and the textural pore formed from the package of the fine particles (*scale bar*=100 nm)
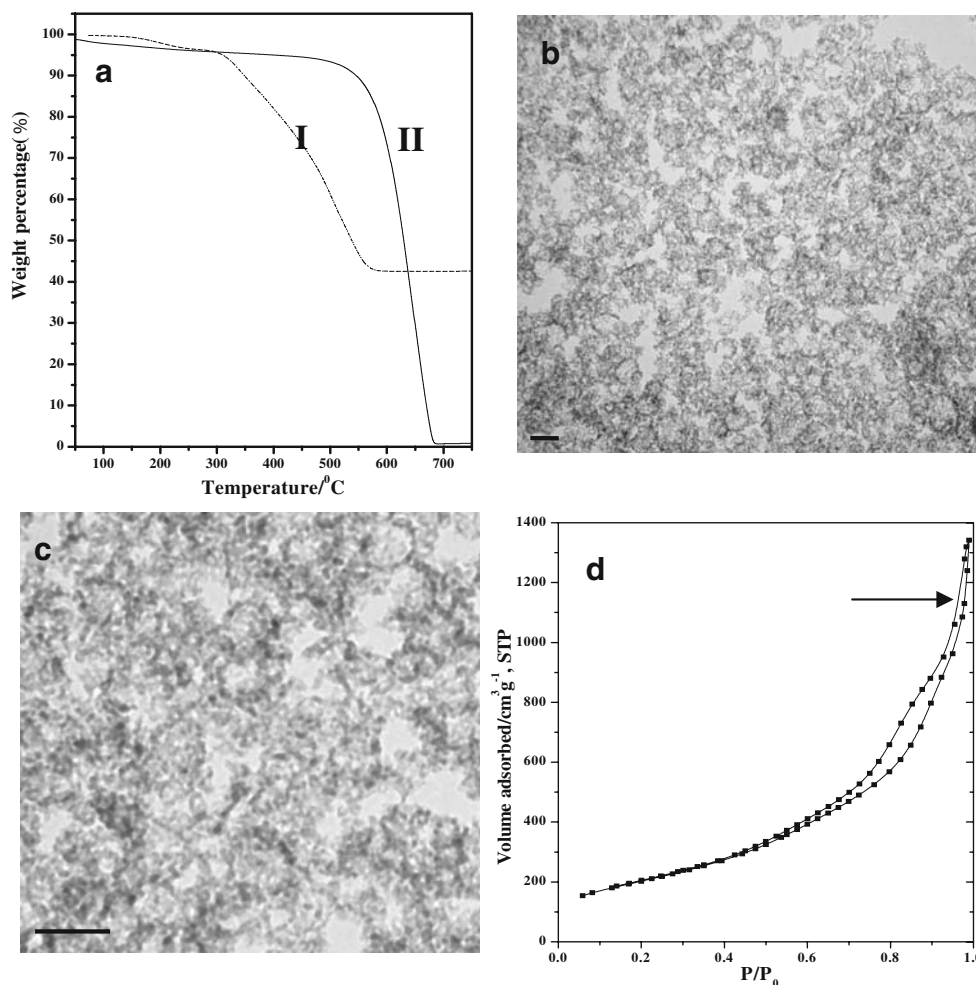
adsorption–desorption isotherm with a capillary condensation from mesopores in the carbon shell occurring at P/P_0=0.3 to 0.4 and an additional absorption form the hollow interior of the hollow sphere at $P/P0 \approx 0.9$ (Fig. 2d). By analyzing the adsorption isotherm, the mesoporous carbon hollow spheres have high BET surface area (~1,206 m^2 g^{-1}), large BJH pore size (~2.6 nm) and pore volume (~1.56 cm^3 g^{-1}) [4].

Mesoporous carbon synthesized with gelatin–PF polymer blend

While considering on the green chemistry, the hydrophobic parts of the surfactants degrade slowly under ambient condition. With increasing concern on the environmental and aquatic toxicity from the amphiphilic surfactants [16], using biodegradable reagents to prepare the mesoporous materials is much attractive. According to silica chemistry, gelatin of water-soluble natural protein, which possesses numerous amide groups (–CO–NH$_2$), can also have a high affinity both to aggregate with silanol groups (Si–OH) on the silicate species and to the PF polymer via multiple hydrogen bonds. Herein, a gelatin–PF polymer blend can also be used as a novel template to conveniently prepare the mesoporous carbons as well.

When combining the gelatin–PF polymer blend water/ethanol solution with the silicate solution at pH≈5.0, a PF–gelatin–silica composite was readily generated in few minutes. The TGA curve of the dried PF–gelatin–silica composite reveals that the organic content is around 60 wt % (Fig. 3a). The high organic fraction should be attributed to the embedded gelatin–PF polymer blend. Because the PF–gelatin–silica composite contains the carbonizable PF polymer, the mesoporous carbon can be directly obtained from a pyrolysis under N$_2$ atmosphere and silica removal. From the TGA curve of the resulted mesoporous silica, it is clearly seen that the gelatin–PF blend-made carbon possesses high thermally stable carbon framework (i.e., high decompose temperature at 600–650 °C), and the silica can be almost completely removed (<1.5 wt%). The TEM image of the mesoporous carbon reveals the morphology of the gelatin–PF templated carbon is in broken holow sphere and fine particles (Fig. 3b). sUnder higher magnificition observation, one can see the disordered mesostructure of few nanometers (Fig. 3c). In parallel, the mesoporous carbon sample exhibits a type-IV N$_2$ adsorption–desorption isotherm (Fig. 3d). The mesoporous carbon possesses a type IV adsoption isotherm of a capillary condensation at $P/P_0 \approx 0.8$–0.9 from mesopores and extra adsorption at $P/P_0 \approx 0.95$ from the interior of the broken hollow spheres and textural pore formed from the package of the fine aprticles. Analyzing the adsorption isotherm, the BET surface area is about 783 m^2 g^{-1} and pore size is around

13.7 nm. According to these results, the gelatin–PF polymer blend can be used as an alternative template to synthesize the mesoporous carbons. This method for the formation of mesoporous carbons can avoid some time- and energy-consuming processes included in the typical mesoporous silica-templating method.

Using mesoporous carbon in electric double-layer capacitor

In practice, the electrically conducting mesoporous carbons of high surface area and large pore size can be considered as good material for preparing high-performance electric capacitors [17, 18]. From the analysis of the N$_2$ adsorption–desorption isotherms, we found that the surface area from the microspore of the aforementioned mesoporous carbon samples is very low (<5%). It is supposed that these mesoporous carbon would present different electrochemical performance form the carbons with micropores. Figure 4 displays the specific capacitances of the different mesoporous carbon electrodes at different sweeping rates. The F127–, PEO6000–, gelatin–PF polymer blend templated mesoporous carbons exhibit electric capacitances of 158, 127, and 76 Fg^{-1} in 2.0 M H$_2$SO$_4$ electrolyte solution at scan rate of 1 mVs^{-1}. With an increase in the sweeping rate, the capacitance values gradually decreases. Comparing to the
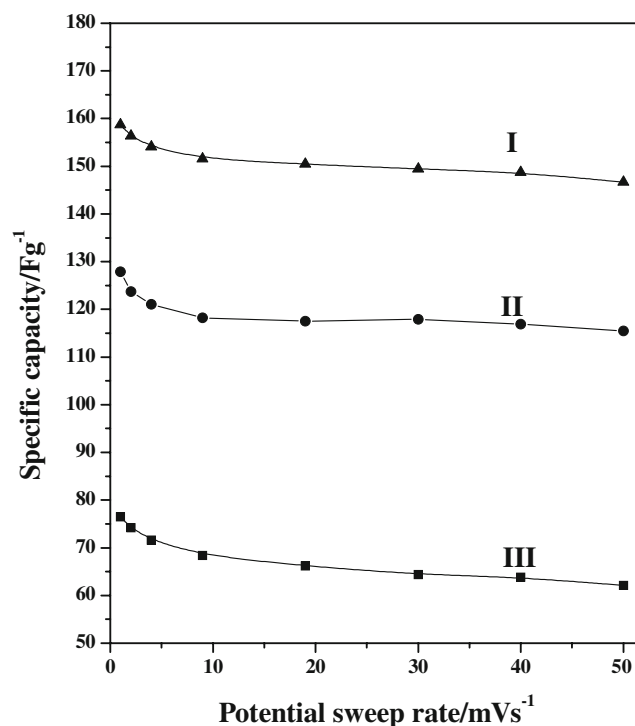
Fig. 4 Variations of the specific capacitance of the different mesoporous carbon electrodes with the potential sweep rate in the two-electrode cyclic voltammetric measurement in 2.0 M H$_2$SO$_4$(aq). *Curve I* F127-PF blend made carbon; *curve II* PEO-PF blend made carbon; *curve III* gelatin–PF blend-made carbon

values at scan rate of 1 mVs^{-1}, the decreasing extent is only about 10% at higher sweeping rate of 50 mVs^{-1}. Distinct from the microporous carbons, such small reduction in the electrochemical performance of all the mesoporous carbons indicates the unrestricted motion of electrolytes in the mesopores, and thus, the formation of the electric double layer should be promoted. The electric capacitances of the mesoporous carbons are dependent on the surface area rather than on the pore size. This is because that the similar chemical properties on the electrochemical performance and mesopores (>2.5 nm) in all the mesoporous carbons are large enough for the limitless ions transport. Hence, the capacitances are solely determined on the surface area of the mesoporous carbons.

In the future, the effects of pH values, water content, and template/silica ratio on the mesostructure and textural properties of the gelatin–PF-templated carbons and silicas will be further explored. To improve mesostructural orderness and surface area of the mesoporous carbons, other experimental factors (such as pH value, solvent properties, silicate concentration, and temperature), which influence interaction strength between the polymer blend and the template-silica self-assembling rate, should be studied.

Conclusion

In brief, we have proposed a new method to conveniently synthesize silica gelator–PF–silica composites by using different polymer blends of Pluronic F127, PEO6000 or gelatin and PF polymer. The synergistic hybrid composite can be transferred to the mesoporous carbon and mesoporous silica as required. This synthetic method only involves the simple mixing of well-defined precursors, the whole procedure to prepare the mesoporous carbon takes only one day, and scaling up of the synthesis of mesoporous carbons is readily accomplished. With a good control of assembling kinetics, one can judiciously select other polymer blends to manufacture the mesoporous carbons with high flexibility in morphologies and misconstrues. These mesoporous carbons of high composition flexibility have potential applications in catalyst, absorbent, sensor, magnetically separable carrier, microcapsules, supercapacitor, drug-delivery, electrode materials in fuel cells, and hard template for mesoporous metal oxides [19–21].

References

1. Lee J, Kim J, Hyeon T (2006) Adv Mater 18:2073
2. Yang H, Zhao D (2005) J Mater Chem 15:1217
3. Kresge CT, Leonowicz ME, Roth WJ, Vartuli JC, Beck JS (1992) Nature 359:710
4. Zhao D, Feng J, Huo Q, Melosh N, Fredrickson GH, Chmelka BF, Stucky GD (1998) Science 279:548
5. Ying JY, Mehnert CP, Wong MS (1999) Angew Chem Int Ed 38:57
6. Kruk M, Jaroniec M, Ko CH, Ryoo R (2000) Chem Mater 12:1961
7. Joo SH, Ryoo R, Kruk M, Jaroniec M (2002) J Phys Chem B 106:4640
8. Kaneda M, Tsubakiyama T, Carlsson A, Sakamoto Y, Ohsuna T, Terasaki O (2002) J Phys Chem B 106:1256
9. Schüth F (2003) Angew Chem Int Ed 42:3604
10. Kruk M, Dufour B, Celer EB, Kowalewski T, Jaroniec M, Matyjaszewski K (2006) Chem Mater 18:1417
11. Stevens MP (1999) Polymer Chemistry. Oxford University, Oxford, New York
12. Iler RK (1979) The chemistry of silica: Solubility, polymerization, colloid and surface properties, and biochemistry. Wiley, New York
13. Arnal PM, Schüth F, Kleitz F (2006) Chem Comm:1203
14. Yeh YQ, Chen BC, Lin HP, Tang CY (2006) Langmuir 22:6
15. Lin HP, Mou CY (2002) Acc Chem Res 35:927
16. Holmberg K, Jönsson B, Kronberg B, Lindman B (2003) Surfactant and polymers in aqueous solution, 2nd edn. Wiley, England
17. Liu HY, Wang KP, Teng H (2005) Carbon 43:559
18. Nikitenko SI, Koltypin Y, Palchik O, Felner I, Xu XN, Gedanken A (2001) Angew Chem Int Ed 40:4447
19. Lee J, Jin S, Hwang Y, Park JG, Park HM, Hyeon T (2005) Carbon 43:2536
20. Kinoshita K (1988) Carbon: Electrochemical and physicochemical properties. Wiley, New York
21. Sun Z, Yuan H, Liu Z, Han B, Zhang X (2005) Adv Mater 17:2993